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MAG-18, no. 6, November 1982, pages 1448-
1450, IEEE, New York, US; N.C. KOON et al.:
"Composition dependence of the coercive force
and microstructure of crystallized amorphous
(Fe_xB_{1-x})_{0.9}Tb_{0.05}La_{0.06} alloys"

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Description

Field of the invention

The present invention relates generally to isotropic permanent magnets and, more particularly, to novel magnets based on FeBR alloys and expressed in terms of FeBR and FeBRM.

In the present disclosure, the term "isotropy" or "isotropic" is used with respect to magnetic properties. In the present invention, R is used as a symbol to indicate rare-earth elements including yttrium Y, M is used as a symbol to denote additional elements such as Al, Ti, V, Cr, Mn, Zr, Hf, Nb, Ta, Mo, Ge, Sb, Sn, Bi, Ni and W, and A is used as a symbol to refer to elements such as copper Cu, phosphorus P, carbon C, sulfur S, calcium Ca, magnesium Mg, oxygen O and silicon Si.

Background of the invention

Permanent magnets are one of functional materials which is practically indispensable for electronic equipments. The permanent magnets currently in use mainly include Alnico® magnets, ferrite magnets, rare earth-cobalt (RCo) magnets and more. With remarkable advances in semiconductor devices in recent years, it is increasingly required to miniaturize and upgrade the parts corresponding to hands and feet or mouths (voice output devices) thereof. The permanent magnets used therefor are required to possess high properties correspondingly.

Although, among permanent magnets, the isotropic permanent magnets are inferior to the anisotropic magnets in certain points in view of performance, the isotropic magnets find good use due to such magnetic properties that no limitation is imposed upon the shape and the direction of magnetization. However, there is left much to be desired in performance. The anisotropic magnets rather than the isotropic magnets are generally put to practical use due to their usually high performance. Although the isotropic magnets are substantially formed of the same material as the anisotropic magnets, for instance, Alnico® magnets, ferrite magnets, MnAl magnets and FeCrCo magnets show a maximum energy product (BH)_{max} of barely 16 kJ/m³ (2 MGOe). SmCo magnets broken down into RCo magnets show a relatively high value on the order of 32–40 kJ/m³ (4–5 MGOe), which is nonetheless only 1/4–1/6 times those of the anisotropic magnets. In addition, the SmCo magnets still offer some problems in connection with practicality, since they are very expensive because of the fact that samarium Sm which is rare in resources is needed, and that it is required to use a large amount, i.e., 50–60 weight % of cobalt Co, the supply of which is uncertain.

It has been desired in the art to use resourceful light rare earth such as, for example, Ce, Nd, Pr and the like in place of Sm belonging to heavy rare earth and substitute Co with Fe. However, it is well-known that light rare earth and Fe do not form intermetallic compounds suitable for magnets, even when they are mutually melted in a homogeneous state, and crystallized by cooling. Furthermore, an attempt made to improve the magnetic force of such light rare earth-Fe alloys through powder metallurgical manners was also unsuccessful (see JP Patent Kokai (Laid-Open) Publication No. 57 (1982)-210934, pp. 6).

On the other hand, it is known that amorphous alloys based on (Fe, Ni, Co)-R can be obtained by melt-quenching. In particular, it has been proposed (in the aforesaid Publication No. 57-210934) to prepare amorphous ribbons from binary alloys based on FeR (as R use is made of Ce, Pr, Nd, Sm, Eu, etc.), especially FeNd and magnetizing the ribbons, whereby magnets are obtained. This process yields magnets having (BH)_{max} of 32–40 kJ/m³ (4–5 MGOe). However, since the resulting ribbons have a thickness ranging from several microns to a few tens microns, they should be laminated or compacted after pulverization in order to obtain magnets of practical bulk. With any existing methods, a lowering of density and a further lowering of magnetic properties would take place. After all, it is unfeasible to introduce improvements in magnetic properties.

In EP-A-101 552 an alloy is disclosed which contains at least one stable compound of the ternary Fe-B-R type having a tetragonal crystal structure and which can be magnetized to become a permanent magnet at room temperature or above.

In EP-A-126 179 a process for producing permanent magnet materials of the Fe-B-R type is disclosed. The process comprises melting and cooling a special composition or reducing a mixture of rare earth oxides and the other metallic materials.

Summary of the invention

It is a principal object of the present invention to provide novel permanent magnets superseding the conventional isotropic permanent magnet materials.

More particularly, the present invention aims at providing isotropic permanent magnets (and materials) having magnetic properties equivalent to, or greater than, those of the conventional products, in which resourceful materials, especially Fe, and resourceful rare-earth elements are mainly used, and in which Sm and the like having problems in resources may not necessarily be used as R.

Furthermore, the present invention aims at providing isotropic permanent magnets having improved magnetic properties such as improved coercive force.

In addition, the present invention aims at providing isotropic permanent magnets which are inexpensive, but are practically of sufficient value.

The present invention also aims at providing a process for the production of these magnets.

The invention is laid down in independent claims 1 and 2.

According to 1st—3rd aspects of the present invention, there are provided magnetically isotropic sintered permanent magnets based on FeBR type compositions. More specifically, according to the first aspect, there is provided an isotropic sintered permanent magnet based on FeBR; according to the second aspect, there is provided an FeBR base magnet, the mean crystal grain size of which is 1—160 μm after sintering; and according to the third aspect, there is provided a process for the production of the FeBR base, isotropic sintered permanent magnets as referred to the first and second aspects.

The 4th—6th aspects of the present invention relate to FeBRM type compositions. More specifically, according to the fourth aspect, there is provided an isotropic permanent magnet based on FeBRM; according to the fifth aspect, there is provided a FeBRM base magnet, the mean crystal grain size of which is 1—100 μm after sintering; and according to the sixth aspect, there is provided a process for the production of the magnets as referred to the fourth and fifth aspects.

The seventh aspect of the present invention is concerned with an allowable level of impurities, which is applicable to the FeBR and FeBRM systems alike, and offers advantages in view of the practical products and the process of production thereof as well as commercial productivity.

In the present disclosure, "%" means "atomic %" unless otherwise specified.

Thus, the isotropic permanent magnets according to the first aspect of the present invention are characterized in that they have a composition (hereinafter referred to "the FeBR composition or system") comprising, in atomic percent, 10—25% of R, 3—23% of boron B and the balance being iron Fe and inevitable impurities, are isotropic, and are obtained as sintered bodies by powder metallurgy.

The isotropic permanent magnets according to the second aspect of the present invention are characterized in that they have the aforesaid FeBR composition, and the sintered bodies have a mean crystal grain size of 1—160 μm after sintering.

The process of production according to the third aspect of the present invention will be described later together with that according to the sixth aspect of the present invention.

The present inventors already invented FeBR base, anisotropic permanent magnets in which Sm and Co were not necessarily used. As a result of intensive studies of isotropic permanent magnets, it has further been found that permanent magnets showing good isotropy can be obtained from the FeBR systems with the application of sintering. Based on such findings, the present invention has been accomplished. The FeBR base, isotropic permanent magnets obtained according to the present invention have properties equivalent to, or greater than, those of the SmCo base, isotropic magnets, and are inexpensive and practically of extremely high value, since expensive Sm may not necessarily be used with no need of using Co.

In the present invention, the term "isotropy" used to indicate one of the properties of the permanent magnets means that they are substantially isotropic, i.e., in a sense that no magnetic field is applied during compacting or forming, and also implies isotropy that may appear by compacting or forming.

The isotropic sintered permanent magnet according to the fourth aspect of the present invention has a composition based on FeBRM (hereinafter referred to "the FeBPM composition or system"), which comprises, in atomic percent, 10—25% of R (provided that R is at least one of rare-earth elements including Y), 3—23% of boron B, no more than given percents (as specified below) of one or two or more of the following additional elements M (exclusive of M=0%, provided that, when two or more additional elements M are added, the combined amounts of M is no more than the maximum value among the values, specified below, of said elements M actually added), and the balance being Fe and inevitable impurities entrained from the process of production:

9.5% Al,	4.7% Ti,	10.5% V,	8.5% Cr,
8.0% Mn,	5.5% Zr,	5.5% Hf,	12.5% Nb,
10.5% Ta,	8.7% Mo,	6.0% Ge,	2.5% Sb,
3.5% Sn	5.0% Bi,	4.7% Ni,	8.8% W.

According to the fifth aspect of the present invention, there is provided the permanent magnet of the fourth aspect in which the sintered body has a mean crystal grain size ranging from about 1 μm to about 100 μm .

The isotropic sintered permanent magnets according to the seventh aspect of the present invention comprises the FeBR and FeBRM compositions in which one or more of A are further contained in given percents. A stands for no more than 3.3% copper Cu, no more than 2.5% sulfur S, no more than 4.0% carbon C, no more than 3.3% phosphorus P, each no more than 4.0% Ca and Mg, no more than 2.0% O and no more than 5.0% Si. It is noted that the combined amount of A is no more than the maximum value among the values specified above of said elements A actually contained, and, when M and A are contained, the sum of M plus A is no more than the maximum value among the values specified above of said elements M and A actually added and contained.

The permanent magnets are obtained as magnetically isotropic sintered bodies, a process for the preparation of which is herein disclosed and characterized in that the respective alloy powders of the FeBR and FeBRM compositions are compacted, followed by sintering (the third and sixth aspects). It is noted that the alloy powders are novel and crystalline rather than amorphous. For instance, the starting alloys are prepared by melting and cooled. The thus cooled alloys are pulverized, compacted under pressure and

sintered resulting in isotropic permanent magnets. Cooling of the molten alloys may usually be done by casting and other cooling manners.

Preferred embodiments of the present invention will now be explained in further detail with reference to the accompanying drawings illustrating examples. It is understood that the present invention is not limited to the embodiments illustrated in the drawings.

Brief description of the drawings

Fig. 1 is a graph showing the relationship between the amount of R (Nd) and coercive force iH_c as well as residual magnetic flux density Br ;

Fig. 2 is a graph showing the relationship between the amount of B and iH_c as well as Br ;

Fig. 3 is a graph showing the relationship between the mean crystal grain size distribution and the coercive force in one example of the present invention;

Fig. 4 is a graph showing the relationship between the amount of some of the elements A and Br in the FeBRA system (77-xFe-8B-15Nd-xA);

Figs. 5 and 6 are graphs showing the amounts of R and B, and Br and iH_c of the FeBRM systems (91-xFe-8B-xNd-1Mo), (84-xFe-xB-15Nd-1Mo), respectively;

Figs. 7 and 8 are graphs showing the relationship between the amount of M and Br in the FeBRxM system (77-xFe-8B-15Nd-xM); and

Fig. 9 is a graph showing the relationship between the mean crystal grain size distribution of sintered bodies and iH_c in the FeBRM systems (75Fe-8B-15Nd-2Al and 76Fe-8B-15Nd-1Mo).

General and first aspect

The FeBR, FeBRA, FeBRM and FeBRMA systems of the present invention are all based on the FeBR system, and are similarly determined in respect of the ranges of B and R.

To meet a coercive force iH_c of no less than 79.6 kA/m (1 kOe) the amount of B should be no less than 3 atomic % (hereinafter "%" stands for the atomic percent in the alloys) in the present invention. An increase in the amount of B increases iH_c but decreases Br (see Figs. 2 and 6). Hence, the amount of B should be no more than 23% to obtain Br of at least 0.3 T (3 kG) to achieve $(BH)_{max}$ of no less than 16 kJ/m³ (2 MGOe).

Figs. 1 and 5 (wherein M denotes Mo) are illustrative of the relationship between the amount of R and iH_c as well as Br in the FeBR and FeBRM systems. As the amount of R increases, iH_c increases, but Br increases then decreases depicting peak. Hence, the amount of R should be no less than 10% to obtain $(BH)_{max}$ of no less than 16 kJ/m³ (2 MGOe), and should be no more than 25% for similar reasons and due to the fact that R is expensive, and so likely to burn that difficulties are involved in technical handling and production.

Preferable with respect to Fe, B and R are the FeBR compositions in which R is 12—20% with the main component being light rare earth such as Nd and/or Pr (the light rare earth amounting to 50% or higher of the overall R), B is 5—18% and the balance is Fe, and the FeBRM compositions wherein the aforesaid ranges hold for Fe, B and R, and M is further within a range providing at least 0.4 T (4 kG) Br , since it is then possible to achieve high magnetic properties represented by $(BH)_{max}$ of no less than 32 kJ/m³ (4 MGOe).

Most preferable with respect to the Fe, B and R are the FeBR compositions in which R is 12—16% with the main component being light rare earth such as Nd or Pr, B is 6—18% and the balance being Fe, and the FeBRM compositions wherein the aforesaid ranges hold for Fe, B and R, and M is within a range providing at least 0.6 T (6 kG) Br , since it is then possible to achieve high properties represented by $(BH)_{max}$ of no less than 56 kJ/m³ (7 MGOe) which has never been obtained in the conventional isotropic permanent magnets.

The present invention is very useful, since the raw materials are inexpensive owing to the fact that resourceful rare earth elements which are resourceful or find no wide use else can be used as R, and that Sm may not necessarily be used, and may not be used as the main ingredient.

Besides Y, R used in the permanent magnets of the present invention include light- and heavy-rare earth, and at least one thereof may be used. That is, use may be made of Nd, Pr, lanthanum La, cerium Ce, terbium Te, dysprosium Dy, holmium Ho, erbium Er, europium Eu, samarium Sm, gadolinium Gd, promethium Pm, thulium Tm, ytterbium Yb, lutetium Lu, Y and the like. It suffices to use light rare earth as R, and particular preference is given to Nd and/or Pr, e.g., no less than 50% of R or mainly of R. Usually, it suffices to use one element as R, but, practically, use may be made of mixtures of two or more elements such as mischmetal, dysprosium, etc. due to easiness in availability. Sm, La, Ce, Gd, Y, etc. may be used in the form of mixtures with light rare earth such as Nd and/or Pr. R may not be pure light rare-earth elements, and contain inevitable impurities entrained from the process of production (other rare-earth elements, Ca, Mg, Fe, Ti, C, O, etc.), as long as such R is industrially available.

The starting B may be pure boron or alloys of B with other constitutional elements such as ferrobore, and may contain as impurities Al, C, silicon Si and more. The same holds for all the aspects of the present invention.

Third aspect (producing process)

The FeBR base permanent magnets disclosed in the prior application are obtained as magnetically anisotropic sintered bodies, and the permanent magnets of the present invention are obtained as similar

sintered bodies, except that they are isotropic. In other words, the isotropic permanent magnets of the present invention are obtained by preparing alloys, e.g., by melting and cooling and pulverizing, compacting and sintering the alloy compacts.

Melting may be carried out in vacuo or in an inert gas atmosphere, and cooling may be effected by, e.g., casting. For casting, a mold formed of copper or other metals may be used. In the present invention, it is desired that a water-cooled type mold is used with the application of a rapid cooling rate to prevent segregation of the ingredients of ingot alloys. After sufficient cooling, the alloys are coarsely ground in a stamp mill or like means and, then, finely pulverized in an attritor, ball mill or like means to no more than about 400 μm preferably 1—100 μm .

In addition to the aforesaid pulverization manner, mechanical pulverization means such as spraying and physicochemical pulverization means such as reducing or electrolytic means may be relied upon for the pulverization of the FeBR base alloys. The alloys of the present invention may be obtained by a so-called direct reduction process in which the oxides of rare earth are directly reduced in the presence of other constitutional elements (e.g., Fe and B or an alloy thereof) with the use of a reducing agent such as Ca, Mg or the like.

The finely pulverized alloys are formulated into a given composition. In this case, the FeBR base or mother alloys may partly be added with constitutional elements or alloys thereof for the purpose of adjusting the composition. The alloy powders formulated to the given composition are compacted under pressure in the conventional manner, and the resultant compact is sintered at a temperature approximately of 900—1200°C, preferably 1050—1150°C for a given period of time. It is possible to obtain the isotropic sintered magnet bodies having high magnetic properties by selecting the sintering conditions (especially temperature and time) in such a manner that the mean crystal grain size of the sintered bodies comes within the predetermined range after sintering. For instance, sintered bodies having a preferable mean crystal grain size can be obtained by compacting the starting alloy powders having a particle size of no more than 100 μm followed by sintering at 1050—1150°C for 30 minutes to 8 hours.

It is noted that sintering is carried out preferably in vacuo or in an inert gas atmosphere which may be vacuo or reduced pressure, e.g., 1.33 Pa (10^{-2} Torr) or less or inert or reducing gas with a purity of 99.9% or higher at 133—101325 Pa (1—760 Torr). During compacting, use may be made of bonding agents such as camphor, paraffin, resins, ammonium chloride or the like and lubricants or compacting aids such as zinc stearate, calcium stearate, paraffin, resins or the like.

Examples (first—third aspects)

The first—third aspects of the present invention will now be elucidated with reference to examples, which are given for the purpose of illustration alone and are not intended to impose any limitation upon the present invention.

Samples of 77Fe-8B-15Nd were prepared by the following steps. In what follows, the unit of purity is weight %.

(1) Referring to the starting materials, electrolytic iron of 99.9% purity was used as Fe; a ferroboron alloy containing 19.4% of B with the balance being Fe and impurities of Al, Si and C as B; and rare earth of 99.7% purity or higher as R (impurities were mainly other rare-earth metals). These materials were formulated into a given atomic ratio, melted and cast in a water-cooled copper mold.

(2) The cooled alloy was coarsely stamp-milled to 0.42 mm (35-mesh) through and, then, finely pulverized for 3 hours in a ball mill to 3—10 μm .

(3) The resultant powders were compacted under a pressure of 14.71×10^7 Pa (1.5 t/cm²).

(4) Sintering was carried out at 1000—1200°C for 1 hour in argon in such a manner that the mean crystal grain size of the sintered body came within a range of 5—30 μm followed by allowing to cool resulting in the samples.

The permanent magnet samples shown in Table 1 prepared by the foregoing steps were measured for the magnetic properties iHc, Br and (BH)max thereof. Table 1 shows the magnetic properties of the individual samples at room temperature.

Within the given ranges of the respective ingredients, iHc of no less than 79.6 kA/m (1 KOe) and Br of no less than 0.3 T (3 kG) were obtained. (BH)max of no less than 16 kJ/m³ (2.0 MGOe) was also obtained. Thus, high magnetic properties are obtained.

It is found that the combination of two or more rare-earth elements is also useful as R. To make a close examination of the relationship between the amounts of R and B and the magnetic properties, a number of samples were prepared by the same steps on the basis of (92-xFe-8B-xNd) systems wherein x=0—35% and Fe-xB-15Nd systems wherein x=0—30%. Figs. 1 and 2 show the iHc and Br measurements of the samples.

TABLE 1

No.	Compositions (at %)	Magnetic properties		
		iHc(kOe)*	Br(kG)*	(BH)max (MGOe)*
C1	85Fe-15Nd	0	0	0
C2	55Fe-30B-15Nd	10.8	1.8	0.7
C3	76Fe-19B-5Pr	0	0	0
C4	53Fe-17B-30Nd	13.5	2.2	1.0
1	82Fe-3B-15Nd	1.7	5.2	2.0
2	80Fe-5B-15Nd	3.4	5.3	4.5
3	77Fe-8B-15Nd	8.5	6.4	8.7
4	68Fe-17B-15Nd	7.2	4.8	4.6
5	70Fe-17B-13Nd	5.3	4.9	4.8
6	65Fe-12B-22Pr	11.0	3.4	2.3
7	63Fe-17B-10Nd-5Pr	7.2	4.7	4.1
8	75Fe-10B-8Nd-7Pr	7.4	6.2	7.8
9	68Fe-19B-8Nd-5Pr-2La	6.6	3.6	2.6
10	75Fe-10B-18Ho	6.0	3.2	2.1
11	70Fe-10B-10Er-5Pr	4.7	3.1	2.2
12	75Fe-10B-10Nd-4Dy-1Sm	3.8	5.3	3.6

*1 kOe=79.6 kA/m

1 kG=0.1 T

1 MGOe=7.96 kJ/m³

Like the ferrite or RCo magnets, the permanent magnets of the FeBR base sintered bodies are the single domain, fine particle type magnets, which give rise to Unpreferable magnet properties without being subjected to once pulverization followed by compacting under pressure and sintering.

With the single domain, fine particle type magnets, no magnetic walls are present within the fine particles, so that the inversion of magnetization is effected only by rotation, which contributes to further increases in coercive force.

To this end, the relationship was investigated between the crystal grain size and the magnetic properties, particularly iHc, of the permanent magnets of the FeBR base sintered bodies according to the present invention, based on the 77Fe-8B-15Nd system. The results are given in Fig. 3.

The mean crystal grain size should be within the range of 1—160 μ m to achieve iHc of no less than 79.6 kA/m (1 kOe), and within a range of 1—110 μ m to achieve iHc of no less than 159.2 kA/m (2 kOe). A range of 1—80 μ m is preferable, and a range of 3—10 μ m is most preferable.

Crystal structure

The present inventors have already disclosed in detail the crystal structure of the magnetic materials and sintered magnets based on the FeBR base alloys in prior European Patent Application No. 83106573.5 (filed on July 5, 1983), the detailed disclosure of which is herewith referred to and incorporated herein, subject to the preponderance of the disclosure recited in this application. The same is also applied to the FeBRM system.

Referring generally to the crystal structure, it is believed that the magnetic material and permanent magnets based on the Fe-B-R alloy according to the present invention can satisfactorily exhibit their own

magnetic properties due to the fact that the major phase is formed by the substantially tetragonal crystals of the Fe-B-R type. The Fe-B-R type alloy is characterized by its high Curie point and it has further been experimentally ascertained that the presence of the substantially tetragonal crystals of the Fe-B-R type contributes to the exhibition of magnetic properties. The contribution of the Fe-B-R base tetragonal system alloy to the magnetic properties is unknown in the art, and serves to provide a vital guiding principle for the production of magnetic materials and permanent magnets having high magnetic properties as aimed at in the present invention.

The tetragonal system of the Fe-B-R type alloys according to the present invention has lattice constants of a_0 : about 0.88 nm (8.8 Å) and c_0 : about 1.22 nm (12.2 Å). It is useful where this tetragonal system compounds constitute the major phase of the Fe-B-R type magnets, i.e., it should occupy 50 vol.% or more of the crystal structure in order to yield practical and good magnetic properties.

Besides the suitable mean crystal grain size of the Fe-B-R base alloys as discussed hereinabove the presence of a Rare earth (R) rich phase (i.e., including about 50 at % of R) serves to yielding of good magnetic properties, e.g., the presence of 1 vol.% or more of such R-rich phase is very effective.

The Fe-B-R tetragonal system compounds are present in a wide compositional range, and may be present in a stable state also upon addition of certain elements other than R, Fe and B. The magnetically effective tetragonal system may be "substantially tetragonal" which term comprises ones that have a slightly deflected angle between a, b and c axes, e.g., within about 1°, or ones that have a_0 slightly different from b_0 , e.g., within about 1%.

The same is applied to the FeBRM system.

The aforesaid fundamental tetragonal system compounds are stable and provide good permanent magnets, even when they contain up to 1% of H, Li, Na, K, Be, Sr, Ba, Ag, Zn, N, F, Se, Te, Pb, or the like.

As mentioned above, contribution of the Fe-B-R type tetragonal system compounds to the magnetic properties have been entirely unknown in the art. It is thus new fact that high properties suitable for permanent magnets are obtained by forming the major phases with these new compounds.

In the field of R-Fe alloys, it has been reported to prepare ribbon magnets by melt-quenching. However, the invented magnets are different from the ribbon magnets in the following several points. That is to say, the ribbon magnets can exhibit permanent magnetic properties in a transition stage from the amorphous or metastable crystal phase to the stable crystal state. Reportedly, the ribbon magnets can exhibit high coercive force only if the amorphous state still remains, or otherwise metastable Fe_3B and R_6Fe_{23} are present as the major phases. The invented magnets have no signs of any alloy phase remaining in the amorphous state, and the major phases thereof are not Fe_3B and R_6Fe_{23} .

When the magnets of the present invention are prepared, use may be made of granulated powders (on the order of several tens-several hundreds μm) obtained by adding binders and lubricants to the alloy powders. The binders and lubricants are not usually employed for the forming of anisotropic magnets, since they disturb orientation. However, they can be incorporated into the magnets of the present invention, since the inventive magnets are isotropic. Furthermore, the incorporation of such agents would possibly result in improvements in the efficiency of compacting and the strength of the compacted bodies.

In preferred embodiments, the isotropic permanent magnets obtained according to the present invention have the magnetic properties higher than those of all the existing isotropic permanent magnets and, moreover, do not require to rely upon expensive ingredients such as Sm and Co. The present invention is also highly advantageous in that it is possible to manufacture magnet products of practically sufficient bulk that is by no means achieved in the proposed amorphous ribbon process.

As stated in detail in the foregoing, the FeBR base isotropic permanent magnets according to the first—third aspects of the present invention give high magnetic properties, making use of inexpensive R materials such as light rare earth (especially Nd, Pr, etc.), particularly various mixtures of light- and heavy-rare earth.

Fourth aspect

According to the fourth aspect of the present invention, additional elements M are added to the FeBR base alloys as disclosed in the first—third aspects to contemplate improving in principle the coercive force iH_c thereof. Namely, the incorporation of M gives rise to a steep increase in iH_c upon increase in the amount of B or R. Generally, as B or R increases Br rises and decreases after depicting a maximum value, wherein M brings about increase of iH_c just in a maximum range of Br. As M, use may be made of one or more of Al, Ti, V, Cr, Mn, Zr, Hf, Nb, Ta, Mo, Ge, Sb, Sn, Bi, Ni and W. In general, the coercive force iH_c drops with increases in temperature. However, it is possible to increase iH_c at normal temperature by the addition of M, so that no demagnetization would take place upon exposure to elevated temperatures. However, as the amount of M increases, there is a lowering of Br and, resulting in a lowering of $(BH)_{max}$, since M is(are) a nonmagnetic element(s) (save Ni). The M-containing alloys are very useful in recently increasing applications where higher iH_c is needed even at the price of slightly reduced $(BH)_{max}$, provided that $(BH)_{max}$ is no less than 16 kJ/m^3 (2 MGOe).

To study the effect of the addition of M upon Br, experiments were conducted in varied amounts of M. The results are shown in Figs. 7 and 8.

It is preferred to make Br no less than 0.3 T (3 kG) so as to make $(BH)_{max}$ equivalent to, or greater than,

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about 16 kJ/m³ (2 MGOe), the level of hard ferrite. As shown in Figs. 7 and 8, the upper limits of M are as follows:

5	9.5% Al,	4.7% Ti,	10.5% V,	8.5% Cr,
	8.0% Mn,	5.5% Zr,	5.5% Hf,	12.5% Nb,
	10.5% Ta,	8.7% Mo,	6.0% Ge,	2.5% Sb,
	3.5% Sn,	5.0% Bi,	4.7% Ni,	8.8% W.

When two or more elements M are added, the resulting properties appear by way of the synthesis of the properties of the individual elements, which varies depending upon the proportion thereof. The amounts of the individual elements M are within the aforesaid ranges, and the combined amount thereof is no more than the maximum value determined with respect to the individual elements which are actually added.

The addition of M incurs a gradual lowering of residual magnetization Br. Hence, according to the present invention, the amount of M is determined such that the obtained magnets have a Br value equivalent to, or greater than, that of the conventional hard ferrite magnets and a coercive force equivalent to, or greater than, that of the conventional products. Preferable amounts of M may be determined by selecting the amounts of M in which, e.g., Br of no less than 0.4 T (4.0 kG) and no less than 0.6 T (6.0 kG) or any desired value between Br of 0.2—0.65 T (2—6.5 kG) or higher is obtained as shown in Figs. 7 and 8.

Fundamentally, the addition of M has an effect upon the increase in coercive force iHc, which, in turn, increases the stability and, hence, the use of magnets.

Preferred is a range of M as hereinbelow specified for obtaining Br of 0.4 T (4 kG) or higher:

25	7.8% Al,	3.8% Ti,	7.8% V,	6.9% Cr,	
	6.9% Mn,	4.8% Zr,	4.5% Hf,	10.0% Nb,	
	8.8% Ta,	7.6% Mo,	5.0% Ge,	2.0% Sb,	and
	2.7% Sn,	4.2% Bi,	3.8% Ni,	7.9% W,	

wherein the same is applied when two or more of M are added.

More preferred is a range of M as hereinbelow specified for obtaining Br of 0.6 T (6 kG) or higher:

35	3.4% Al,	1.3% Ti,	3.4% V,	1.5% Cr,	
	2.1% Mn,	1.9% Zr,	1.7% Hf,	2.8% Nb,	
	3.0% Ta,	2.8% Mo,	1.6% Ge,	0.5% Sb,	and
	0.7% Sn,	1.9% Bi,	1.3% Ni,	3.7% W,	

wherein the same is applied when two or more of M are added. The range of M is most preferably 0.1—3.7% to achieve (BH)max of about 56 kJ/m³ (7 MGOe), taking into consideration the effects thereof upon the increase in iHc and the lowering of Br as well as upon (BH)max. As M, V, Nb, Ta, Mo, W, Cr and Al are preferred, while a minor amount of Al is particularly useful.

The relationship between the amount of M and the coercive force has been established by way of a wide range of experiments.

Fifth aspect

According to the fifth aspect of the present invention, it is clarified that good magnetic properties are achieved when the FeBRM base sintered bodies have a mean crystal grain size within a given constant range. That is, iHc of no less than 79.6 kA/m (1 kOe) is satisfied, when the mean crystal grain size of the sintered bodies is in a range of about 1 to about 100 μm. A preferable range is 1—80 μm and a most preferable range is 2—30 μm wherein further enhanced iHc is obtained.

This is substantially true of the FeBRM systems and the FeBRMA systems alike.

Sixth aspect

Producing process is substantially the same as the third aspect except for preparation of the starting alloys or alloy powders. The additional elements M may be added to the FeBR base alloy(s) or may be prepared as FeBRM alloys. Minor amount of alloys of the constitutional elements of Fe, B, R and M may be added to the mother alloys for formulating the final composition.

Seventh aspect

The permanent magnets according to the seventh aspect of the present invention may permit the entrainment of the elements A in quantities in or below given %. A includes Cu, S, C, P, Ca, Mg, O, Si and the like. When the FeBR and FeBRM base magnets are industrially prepared, such elements may often be entrained therein from the raw materials, the process of production, etc. For instance, when FeB is used as the raw material, S and P may often be entrained. In most cases, C remains as the residue of organic binders (compacting-aids) used in the process of powder metallurgy. Cu is frequently contained in cheap

raw materials. Ca and Mg may easily be entrained from reducing agents. It has been observed that as the amount of entrained A increases, the residual magnetic flux density Br tends to drop.

As a result, when the amounts of S, C, P and Cu are no more than 2.5%, 4.0%, 3.3% and 3.3%, respectively, the obtained properties (Br) are equal to, or greater than, those of hard ferrite (see Fig. 4). The allowable upper limits of O, Ca, Mg and Si are 2%, 4.0%, 4.0% and 5.0%, respectively.

When two or more elements A are entrained in the magnets, the properties of the individual elements are synthesized, and the total amount thereof is no more than the maximum value of the values, specified above, of the actually entrained A. Within this range, Br is equal to, or greater than, that of hard ferrite.

In the case of the FeBRMA base magnets in which the isotropic permanent magnets based on FeBRM contain further A, the combined amount of (M+A) is no more than the highest upper limit of the upper limits of the elements actually added and entrained, as is substantially the case with two or more M or A. This is because both M and A are apt to decrease Br. In the case of the addition of two or more M and the entrainment of two or more A, the resulting Br property appears through the synthesis of the effects of the individual elements upon Br, which varies depending upon the proportion thereof.

Al may be entrained from a refractory such as an alumina crucible into the alloys, but offers no disadvantage since it is useful as M. M and A have no essential influence upon Curie point Tc, as long as they are within the presently claimed compositional range.

Examples (fourth—sixth aspects)

The fourth—sixth aspects of the present invention will now be explained in further detail with reference to examples, which are given for the purpose of illustration alone, and are not intended to place any limitation on the invention.

Prepared were the samples based on FeBRM and FeBRMA base alloys containing the given additional elements in the following manner.

(1) Referring to the starting materials, electrolytic iron of 99.9% purity was used as Fe; ferroboration alloys and boron of 99% purity used as B; and Nd, Pr, Dy, Sm, Ho, Er and Ce each of 99% purity or higher used as R (impurities were mainly other rare-earth metals). The starting materials were melted by high-frequency melting, and cast in a water-cooled copper mold. As M use was made of Ti, Mo, Bi, Mn, Sb, Ni, Ta, Sn and Ge each of 99% purity, W of 98% purity, Al of 99.9% purity, and Hf of 95% purity. Furthermore, ferrovanadium containing 81.2% of V, ferroniobium containing 67.6% of Nb, ferrochromium containing 61.9% of Cr and ferrozirconium containing 75.5% of Zr were used as V, Nb, Cr and Zr, respectively.

Where the elements A were contained, use was made of S of 99% purity or higher, ferrophosphorus containing 26.7% of P, C of 99% purity or higher, and electrolytic Cu of 99.9% purity or higher.

The unit of purity hereinabove is % by weight.

(2) Pulverization.

Coarse pulverization was carried out to 0.420 mm (35-mesh through) in a stamp mill, and fine pulverization done in a ball mill for 3 hours to 3—10 μ m.

(3) Compacting was effected under a pressure of 14.71×10^7 Pa (1.5 t/cm²).

(4) Sintering was carried out at 1000—1200°C for 1 hour in argon in such a manner that the mean crystal grain size of the sintered bodies came within a range of 5—10 μ m followed by cooling down.

To investigate the magnet properties of the thus obtained samples having a variety of compositions, iHc, Br and (BH)max thereof were measured. Table 2 enumerates the permanent magnet properties, iHc, Br and (BH)max of the typical samples. Although not indicated numerically in the table, the balance is Fe.

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TABLE 2-1

No.	Compositions (at %)	Magnetic properties		
		iHc(kOe)*	Br(kG)*	(BH)max (MGOe)*
1	Fe-8B-15Nd	8.5	6.4	8.7
2	Fe-8B-10Nd-5Pr	5.4	4.8	4.3
3	Fe-17B-15Nd	7.2	4.8	4.6
C4	Fe-15Nd-5Al	<1	<1	<1
C5	Fe-20Nd-3W	<1	<1	<1
C6	Fe-30B-15Nd-5Al	<1	<1	<1
C7	Fe-8B-30Nd-5Cr	>10	<1	<1
C8	Fe-17B-5Nd-2Al-1W	<1	<1	<1
C9	Fe-2B-15Nd-1W	1.2	3.0	<1
10	Fe-8B-15Nd-1Ti	9.2	5.9	6.9
11	Fe-8B-15Nd-3V	9.6	4.3	3.7
12	Fe-8B-15Nd-1Nb	10.0	6.1	7.9
13	Fe-8B-15Nd-0.5Nb	9.5	6.3	8.4
14	Fe-8B-15Nd-5Nb	11.0	4.4	3.9
15	Fe-8B-15Nd-2Ta	9.8	5.6	6.0
16	Fe-8B-15Nd-2Cr	10.1	4.3	3.7
17	Fe-8B-15Nd-0.5Mo	9.4	6.3	8.2
18	Fe-8B-15Nd-1Mo	10.2	5.8	6.8
19	Fe-8B-15Nd-5Mo	11.0	4.2	3.5
20	Fe-8B-15Nd-0.5W	10.5	5.9	7.4

Fe=balance Fe

*1 kOe=79.6 kA/m

1 kG=0.1 T

1 MGOe=7.96 kJ/m³

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TABLE 2-2

No.	Compositions (at %)	Magnetic properties		
		iHc(kOe)*	Br(kG)*	(BH)max (MGOe)*
21	Fe-8B-15Nd-1W	12.3	5.8	7.0
22	Fe-8B-15Nd-5W	13.3	4.0	3.1
23	Fe-8B-15Nd-3Mn	9.0	4.3	3.7
24	Fe-8B-15Nd-3Ni	8.4	4.9	4.7
25	Fe-8B-15Nd-0.5Al	9.7	5.9	7.3
26	Fe-8B-15Nd-2Al	11.5	5.3	5.6
27	Fe-8B-15Nd-5Al	11.9	4.2	3.4
28	Fe-8B-15Nd-0.5Ge	8.9	5.7	6.2
29	Fe-8B-15Nd-1Sn	11.8	4.7	4.4
30	Fe-8B-15Nd-1Sb	10.1	4.6	4.1
31	Fe-8B-15Nd-1Bi	10.2	5.3	5.7
32	Fe-8B-15Nd-3Ti	9.1	4.7	4.4
33	Fe-8B-15Nd-1Hf	8.9	4.4	3.9
34	Fe-8B-15Nd-1.5Zr	10.3	4.7	4.3
35	Fe-8B-15Pr-2Mo	8.8	5.4	6.0
36	Fe-17B-15Pr-1Hf-2Al	9.6	3.4	2.3
37	Fe-8B-10Nd-5Pr-2Nb-2Ti	9.9	4.1	3.4
38	Fe-8B-20Nd-0.5Mo-0.5W-1Ti	14.0	3.6	2.5
39	Fe-8B-12Nd-3Dy-0.5Nb-0.5Ti	9.2	4.1	3.4
40	Fe-10B-14Nd-1Sm-1Al-0.5W	12.2	4.3	3.7

Fe=balance Fe

*1 kOe=79.6 kA/m

1 kG=0.1 T

1 MGOe=7.96 kJ/m³

TABLE 2-3

No.	Compositions (at %)	Magnetic properties		
		iHc(kOe)*	Br(kG)*	(BH)max (MGoe)*
41	Fe-12B-10Nd-5Ho-2Nb	7.5	4.7	4.2
42	Fe-7B-19Nd-5Er-1Ta	11.2	5.3	5.0
43	Fe-8B-11Nd-4Ce-1Al	5.3	4.9	4.8
44	Fe-10B-15Nd-1Al-1P	8.6	4.4	3.4
45	Fe-7B-16Nd-1Ti-1C	6.8	3.7	2.6
46	Fe-8B-15Nd-1W-0.5Cu	3.8	5.3	5.1
47	Fe-9B-14Nd-1Si-1S	5.1	3.4	2.1

Fe=balance Fe

*1 kOe=79.6 kA/m

1 kG=0.1 T

1 MGoe=7.96 kJ/m³

Although the alloys containing as R, Nd, Pr, Dy and Sm are exemplified, 15 rare-earth elements (Y, Ce, Sm, Eu, Tb, Dy, Er, Tm, Yb, Lu, Nd, Pr, Gd, Ho and La) show a substantially similar tendency. However, the alloys containing Nd and Pr as the main component are much more useful than those containing scarce rare earth (Sm, Y, heavy rare earth) as the main ingredient, since rare earth ores abound relatively with Nd and Pr and, in particular, Nd does not still find any wide use.

In Table 2, samples Nos. 4 through 9 inclusive are reference examples for the permanent magnets of the present invention.

Out of the examples of the present invention shown in Table 2, examination was made of the relationship between the coercive force iHc and the mean crystal grain size D μ m after sintering of Nos. 18 and 26. The results are shown in Fig. 9. Even with the same magnet, the coercive force varies depending upon the crystal grain size. Good results are obtained in a range of 2—30 μ m and a peak appears in a range of approximately 3—10 μ m.

From this, it is concluded that the grading of mean crystal grain sizes is required and preferred to take full advantage of the permanent magnets of the present invention. The graph of Fig. 9 was based on the data obtained in a similar manner as already mentioned, provided however that the particle size of alloy powders and the crystal grain size after sintering were varied.

The permanent magnets of the present invention can be prepared with the use of commercially available materials, and it is very advantageous to use the light rare-earth elements as the key component of magnet materials. While heavy rare earth is generally of less industrial value due to the fact that it is resourceless and expensive, it may be used alone or in combination with light rare earth.

The increase in coercive force contributes to the stabilization of magnetic properties. Hence, the addition of M makes it feasible to obtain permanent magnets, which are substantially very stable and show a high energy product. In addition, the entrainment of the elements A within the given range offers a practical advantage in view of the industrial production of permanent magnets.

As described in detail in the foregoing, the present invention provides permanent magnets comprising magnetically isotropic sintered bodies based on FeBR, FeBRM, FeBRA and FeBRMA base alloys, whereby magnetic properties equal to, or greater than, those achieved in the prior art are realized particularly without recourse to resourceless or expensive materials. In other words, the isotropic sintered bodies of the present invention provide practical permanent magnets, which are excellent in view of resources, prices and magnetic properties, using as R light rare earth such as Nd and Pr. Thus, the present invention is industrially of high value.

Modifications apparent in the art may be made without departing from the gist of the present invention as disclosed and claimed:

Claims

1. An isotropic sintered permanent magnet consisting essentially of, in atomic percent, 10—25% of R wherein R represents at least one of rare-earth elements including Y, 3—23% of B and the balance being Fe

and inevitable impurities, in which the sintered particles have a mean crystal grain size of 1—160 μm , mean crystal grain sizes up to 80 μm being excluded.

2. A process for preparing isotropic sintered permanent magnets comprising the steps of melting and preparing alloys comprising, in atomic percent, 10—25% of R wherein R represents at least one of rare-earth elements including Y, 3—23% of B and the balance being Fe and inevitable impurities, cooling the resultant molten alloys, pulverizing the resultant alloys, compacting the pulverized alloys, and sintering the resultant compact under such conditions that the sintered particles have a mean crystal grain size of 1—160 μm , mean crystal grain sizes up to 80 μm being excluded.

3. A magnet as defined in Claim 1, in which, of said impurities, Cu is no more than 3.3%, S is no more than 2.5%, C is no more than 4.0%, P is no more than 3.3%, Ca is no more than 4.0%, Mg is no more than 4.0%, O is no more than 2.0%, and Si is no more than 5.0%, wherein, when two or more of said elements are applied, the combined amount of said elements is limited to the highest value of one of said individual elements added.

4. A process as defined in Claim 2, in which, of said impurities, Cu is no more than 3.3%, S is no more than 2.5%, C is no more than 4.0%, P is no more than 3.3%, Ca is no more than 4.0%, Mg is no more than 4.0%, O is no more than 2.0%, and Si is no more than 5.0%, wherein, when two or more of said elements are applied, the combined amount of said elements is limited to the highest value of one of said individual elements added.

5. A magnet according to Claim 1, further comprising at least one additional element M, where M stands for

	no more than 9.5% Al,	no more than 4.7% Ti,
	no more than 10.5% V,	no more than 8.5% Cr,
	no more than 8.0% Mn,	no more than 5.5% Zr,
25	no more than 5.5% Hf,	no more than 12.5% Nb,
	no more than 10.5% Ta,	no more than 8.7% Mo,
	no more than 6.0% Ge,	no more than 2.5% Sb,
	no more than 3.5% Sn,	no more than 5.0% Bi, and
	no more than 4.7% Ni,	no more than 8.8% W,

30 wherein, when two or more of said elements M are applied, the combined amount of M is limited to the highest value of one of the individual elements M added.

6. A magnet according to Claim 5, wherein the sintered particles have a mean crystal grain size of about 1—100 μm , mean crystal grain sizes up to 80 μm being excluded.

35 7. A process according to Claim 2, further comprising at least one additional element M, where M stands for

	no more than 9.5% Al,	no more than 4.7% Ti,
	no more than 10.5% V,	no more than 8.5% Cr,
	no more than 8.0% Mn,	no more than 5.5% Zr,
40	no more than 5.5% Hf,	no more than 12.5% Nb,
	no more than 10.5% Ta,	no more than 8.7% Mo,
	no more than 6.0% Ge,	no more than 2.5% Sb,
	no more than 3.5% Sn,	no more than 5.0% Bi, and
45	no more than 4.7% Ni,	no more than 8.8% W,

wherein, when two or more of said elements M are applied, the combined amount of M is limited to the highest value of one of the individual elements M added.

8. A process according to Claim 7, wherein sintering is carried out under such conditions that the sintered particles have a mean crystal grain size of 1—100 μm , mean crystal grain sizes up to 80 μm being excluded.

9. A magnet as defined in Claim 5 or 6, in which, of said impurities (A), Cu is no more than 3.3%, S is no more than 2.5%, C is no more than 4.0%, P is no more than 3.3%, Ca is no more than 4.0%, Mg is no more than 4.0%, O is no more than 2.0%, and Si is no more than 5.0%, wherein, when one or two or more of said M and A, respectively, are applied, the combined amount of (M+A) is limited to the highest value of one of the individual elements M and A added.

10. A process as defined in Claim 7 or 8, in which, of said impurities, Cu is no more than 3.3%, S is no more than 2.5%, C is no more than 4.0%, P is no more than 3.3%, Ca is no more than 4.0%, Mg is no more than 4.0%, O is no more than 2.0%, and Si is no more than 5.0%, wherein, when one or two or more of said elements M and A, respectively, are applied, the combined amount of (M+A) is limited to the highest value of one of the individual elements M and A added.

11. A magnet as defined in Claim 1, 5 or 6, in which, in atomic percent, R is 12—20%, and B is 5—18%.

12. A magnet as defined in Claim 11, in which, R is 12—16%, and B is 6—18%.

13. A process as defined in Claim 2, 7 or 8, in which, in atomic percent, R is 12—20%, and B is 5—18%.

65 14. A process as defined in Claim 13, in which R is 12—16%, and B is 6—18%.

Patentansprüche

1. Isotroper, gesinterter Permanentmagnet, bestehend im wesentlichen aus, in Atom-%, 10—25% R, worin R wenigstens ein Element der Seltenen Erden einschließlich Y darstellt, 3—23% B und Rest Fe sowie
5 unvermeidbaren Verunreinigungen, in dem die gesinterten Partikel eine mittlere Kristallkorngröße von 1—160 µm aufweisen, wobei mittlere Kristallkorngröße bis zu 80 µm ausgeschlossen sind.

2. Verfahren zur Herstellung isotroper, gesinteter Permanentmagnete, enthaltend die Schritte Schmelzen und Herstellen von Legierungen, die, in Atom-%, 10—25% R, worin R wenigstens ein Element der Seltenen Erden einschließlich Y darstellt, 3—23% B und Rest Fe sowie unvermeidbare Ver-
10 unreinigungen enthalten, Abkühlen der erhaltenen geschmolzenen Legierungen, Pulverisieren, der erhaltenen Legierungen, Verdichten der pulverisierten Legierungen und Sintern des erhaltenen verdichteten Körpers unter solchen Bedingungen, daß die gesinterten Partikel eine mittlere Kristallkorngröße von 1—160 µm aufweisen, wobei mittlere Kristallkorngrößen bis zu 80 µm ausgeschlossen sind.

3. Magnet nach Anspruch 1, in dem von den genannten Verunreinigungen Cu nicht mehr als 3,3%, S
15 nicht mehr als 2,5%, C nicht mehr als 4,0%, P nicht mehr als 3,3%, Ca nicht mehr als 4,0%, Mg nicht mehr als 4,0%, O nicht mehr als 2,0% und Si nicht mehr als 5,0% ausmachen, wobei dann, wenn zwei oder mehr der genannten Elemente verwendet werden, die Gesamtmenge dieser Elemente auf den höchsten Wert eines der zugegebenen einzelnen Elemente begrenzt ist.

4. Verfahren nach Anspruch 2, in dem von den genannten Verunreinigungen Cu nicht mehr als 3,3%, S
20 nicht mehr als 2,5%, C nicht mehr als 4,0%, P nicht mehr als 3,3%, Ca nicht mehr als 4,0%, Mg nicht mehr als 4,0%, O nicht mehr als 2,0% und Si nicht mehr als 5,0% ausmachen, wobei dann, wenn zwei oder mehr der genannten Elemente verwendet werden, die Gesamtmenge dieser Elemente auf den höchsten Wert eines der zugegebenen einzelnen Elemente begrenzt ist.

5. Magnet nach Anspruch 1, weiterhin enthaltend wenigstens ein zusätzliches Element M, wobei M für
25

nicht mehr als 9,5% Al,	nicht mehr als 4,7% Ti,	
nicht mehr als 10,5% V,	nicht mehr als 8,5% Cr,	
nicht mehr als 8,0% Mn,	nicht mehr als 5,5% Zr,	
nicht mehr als 5,5% Hf,	nicht mehr als 12,5% Nb,	
30 nicht mehr als 10,5% Ta,	nicht mehr als 8,7% Mo,	
nicht mehr als 6,0% Ge,	nicht mehr als 2,5% Sb,	
nicht mehr als 3,5% Sn,	nicht mehr als 5,0% Bi,	und
nicht mehr als 4,7% Ni,	nicht mehr als 8,8% W,	

35 steht, wobei dann, wenn zwei oder mehr der genannten Elemente M verwendet werden, die Gesamtmenge von M auf den höchsten Wert eines der zugegebenen einzelnen Elemente M begrenzt ist.

6. Magnet nach Anspruch 5, worin die gesinterten Partikel eine mittlere Kristallkorngröße von etwa 1—100 µm aufweisen, wobei mittlere Kristallkorngrößen bis zu 80 µm ausgeschlossen sind.

7. Verfahren nach Anspruch 2, weiterhin enthaltend wenigstens ein zusätzliches Element M, wobei M
40 für

nicht mehr als 9,5% Al,	nicht mehr als 4,7% Ti,	
nicht mehr als 10,5% V,	nicht mehr als 8,5% Cr,	
nicht mehr als 8,0% Mn,	nicht mehr als 5,5% Zr,	
45 nicht mehr als 5,5% Hf,	nicht mehr als 12,5% Nb,	
nicht mehr als 10,5% Ta,	nicht mehr als 8,7% Mo,	
nicht mehr als 6,0% Ge,	nicht mehr als 2,5% Sb,	
nicht mehr als 3,5% Sn,	nicht mehr als 5,0% Bi,	und
nicht mehr als 4,7% Ni,	nicht mehr als 8,8% W,	

50 steht, wobei dann, wenn zwei oder mehr der genannten Elemente M verwendet werden, die Gesamtmenge von M auf den höchsten Wert eines der angegebenen einzelnen Elemente M begrenzt ist.

8. Verfahren nach Anspruch 7, worin das Sintern unter solchen Bedingungen durchgeführt wird, daß die gesinterten Partikel eine mittlere Kristallkorngröße von 1—100 µm aufweisen, wobei mittlere
55 Kristallkorngrößen bis zu 80 µm ausgeschlossen sind.

9. Magnet nach Anspruch 5 oder 6, in dem von den genannten Verunreinigungen (A) Cu nicht mehr als 3,3%, S nicht mehr als 2,5%, C nicht mehr als 4,0%, P nicht mehr als 3,3%, Ca nicht mehr als 4,0%, Mg nicht mehr als 4,0%, O nicht mehr als 2,0% und Si nicht mehr als 5,0% ausmachen, wobei dann, wenn ein oder zwei oder mehr der genannten Elemente M bzw. A verwendet werden, die Gesamtmenge an (M+A) auf
60 den höchsten Wert eines der angegebenen Elemente M und A begrenzt ist.

10. Verfahren nach Anspruch 7 oder 8, in dem von den genannten Verunreinigungen Cu nicht mehr als 3,3%, S nicht mehr als 2,5%, C nicht mehr als 4,0%, P nicht mehr als 3,3%, Ca nicht mehr als 4,0%, Mg nicht mehr als 4,0%, O nicht mehr als 2,0% und Si nicht mehr als 5,0% ausmachen, wobei dann, wenn ein oder zwei oder mehr der genannten Elemente M bzw. A verwendet werden, die Gesamtmenge (M+A) auf den
65 höchsten Wert eines der zugegebenen einzelnen Elemente M und A begrenzt ist.

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11. Magnet nach Anspruch 1, 5 oder 6, in dem, in Atom-%, R 12—20% und B 5—18% ausmachen.
 12. Magnet nach Anspruch 11, in dem R 12—16% und B 6—18% ausmachen.
 13. Verfahren nach Anspruch 2, 7 oder 8, in dem, in Atom-%, R 12—20% und B 5—18% ausmachen.
 14. Verfahren nach Anspruch 13, in dem R 12—16% und B 6—18% ausmachen.
 5 15. Magnet nach Anspruch 1, 5 oder 6, in dem R 50% oder mehr an Elementen der leichten Seltenen Erden enthält.
 16. Magnet nach Anspruch 15, in dem R 50% oder mehr an Nd und/oder Pr enthält.
 17. Magnet nach Anspruch 16, in dem R etwa 15 Atom-% und B etwa 8 Atom-% ausmachen.
 18. Verfahren nach Anspruch 2, 7 oder 8, in dem R 50% oder mehr an Elementen der leichten Seltenen
 10 Erden enthält.
 19. Verfahren nach Anspruch 18, in dem R 50% oder mehr an Nd und/oder Pr enthält.
 20. Verfahren nach Anspruch 19, in dem R etwa 15 Atom-% und B etwa 8 Atom-% ausmachen.
 21. Magnet nach Anspruch 1, 5 oder 6, in dem die Hauptphase von einer Legierung des FeBR-Typs gebildet wird, die eine im wesentlichen tetragonale Struktur aufweist.
 15 22. Magnet nach Anspruch 1, 5 oder 6, der 1 Vol-% oder mehr einer an Seltenen Erden reichen Phase enthält.
 23. Magnet nach Anspruch 1, 5 oder 6, der einen (BH)max von nicht weniger als 16 kJ/m³ (2 MGOe) aufweist.
 24. Magnet nach Anspruch 11, der ein (BH)max von nicht weniger als 32 kJ/m³ (4 MGOe) aufweist.
 20 25. Magnet nach Anspruch 12, der ein (BH)max von nicht weniger als 56 kJ/m³ (7 MGOe) aufweist.
 26. Magnet nach Anspruch 5 oder 6, worin die zusätzlichen Elemente M in oder unter den folgenden Werten in Atom-% enthalten sind:

25	7,8% Al, 6,9% Mn, 8,8% Ta, 2,7% Sn,	3,8% Ti, 4,8% Zr, 7,6% Mo, 4,2% Bi,	7,8% V, 4,5% Hf, 5,0% Ge, 3,8% Ni,	6,9% Cr, 10,0% Nb, 2,0% Sb, 7,9% W,	und
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wobei dann, wenn zwei oder mehr der genannten Elemente M verwendet werden, die Gesamtmenge von M auf den höchsten Wert eines der zugegebenen einzelnen Elemente M begrenzt ist.

27. Verfahren nach einem der Ansprüche 7 oder 8, worin die zusätzlichen Elemente M in oder unter den folgenden Werten in Atom-% eingesetzt werden:

35	7,8% Al, 6,9% Mn, 8,8% Ta, 2,7% Sn,	3,8% Ti, 4,8% Zr, 7,6% Mo, 4,2% Bi,	7,8% V, 4,5% Hf, 5,0% Ge, 3,8% Ni,	6,9% Cr, 10,0% Nb, 2,0% Sb, 7,9% W,	und
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wobei dann, wenn zwei oder mehr der genannten Elemente M verwendet werden, die Gesamtmenge von M auf den höchsten Wert eines der zugegebenen einzelnen Elemente M begrenzt ist.

28. Magnet nach Anspruch 12, worin die zusätzlichen Elemente M in oder unter den folgenden Werten in Atom-% enthalten sind:

45	3,4% Al, 2,1% Mn, 3,0% Ta, 0,7% Sn,	1,3% Ti, 1,9% Zr, 2,8% Mo, 1,9% Bi,	3,4% V, 1,7% Hf, 1,6% Ge, 1,3% Ni,	1,5% Cr, 2,8% Nb, 0,5% Sb, 3,7% W,	und
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wobei dann, wenn zwei oder mehr der genannten Elemente M verwendet werden, die Gesamtmenge von M auf den höchsten Wert eines der zugegebenen einzelnen Elemente M begrenzt ist.

29. Verfahren nach Anspruch 14, worin die zusätzlichen Elemente M in oder unter den folgenden Werten in Atom-% verwendet werden:

55	3,4% Al, 2,1% Mn, 3,0% Ta, 0,7% Sn,	1,3% Ti, 1,9% Zr, 2,8% Mo, 1,9% Bi,	3,4% V, 1,7% Hf, 1,6% Ge, 1,3% Ni,	1,5% Cr, 2,8% Nb, 0,5% Sb, 3,7% W,	und
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wobei dann, wenn zwei oder mehr der genannten Elemente M verwendet werden, die Gesamtmenge von M auf den höchsten Wert eines der zugegebenen einzelnen Elemente M begrenzt ist.

30. Magnet nach Anspruch 26, der eine Br von nicht weniger als 0,4 Tesla (4 kG) aufweist.
 31. Magnet nach Anspruch 28, der eine Br von nicht weniger als 0,6 Tesla (6 kG) aufweist.
 32. Magnet nach Anspruch 5 oder 6, in dem M ein oder mehr Elemente, ausgewählt aus der Gruppe bestehend aus V, Nb, Ta, Mo, W, Cr und Al, darstellt.

33. Verfahren nach Anspruch 2, 7 oder 8, worin das Sintern bei einer Temperatur von 900 bis 1200°C durchgeführt wird.

34. Verfahren nach Anspruch 33, worin das Sintern in einer nichtoxidierenden oder reduzierenden Atmosphäre durchgeführt wird.

5 35. Verfahren nach Anspruch 34, worin die genannte Atmosphäre Vakuum oder ein verminderter Druck oder ein Inertgas mit einer Reinheit von 99,9% oder mehr unter einem Druck von 133 bis 101325 Pa (1—760 Torr) ist.

10 Revendications

1. Aimant permanent fritté isotrope, essentiellement constitué, en pourcentages atomiques, de 10 à 25% de R, où R représente au moins un élément des terres rares comprenant Y, 3 à 23% de B, le reste étant du fer et des impuretés inévitables, les particules frittées ayant un diamètre moyen du grain de cristal de 1 à 15 160 µm, des diamètres moyens du grain de cristal jusqu'à 80 µm étant exclus.

2. Procédé de production d'aimants permanents frittés isotropes, qui implique les étapes de fusion et de préparation d'alliages comprenant, en pourcentages atomiques, 10 à 25% de R où R représente au moins l'un des éléments des terres rares y compris Y, 3 à 23% de B et le reste étant du fer et des impuretés inévitables, à refroidir les alliages fondus résultants, à pulvériser les alliages résultants, à compacter les 20 alliages pulvérisés et à fritter la masse compacte résultante dans des conditions choisies de manière que les particules frittées aient un diamètre moyen du grain de cristal de 1 à 160 µm, des diamètres moyens du grain de cristal jusqu'à 80 µm étant exclus.

3. Aimant tel que défini dans la revendication 1, dans lequel, parmi lesdites impuretés, Cu ne représente pas plus de 3,3%, S ne représente pas plus de 2,5%, C ne représente pas plus de 4,0%, P ne 25 représente pas plus de 3,3%, Ca ne représente pas plus de 4,0%, Mg ne représente pas plus de 4,0%, O ne représente pas plus de 2,0% et Si ne représente pas plus de 5,0%, et lorsque deux ou plus de deux desdits éléments sont utilisés, la quantité totale desdits éléments est limitée à la valeur maximale de l'un desdits éléments individuels ajoutés.

4. Procédé suivant la revendication 2, dans lequel, parmi lesdites impuretés, Cu ne représente pas plus de 3,3%, S ne représente pas plus de 2,5%, C ne représente pas plus de 4,0%, P ne représente pas plus de 3,3%, Ca ne représente pas plus de 4,0%, Mg ne représente pas plus de 4,0%, O ne représente pas plus de 2,0% et Si ne représente pas plus de 5,0%, et lorsque deux ou plus de deux desdits éléments sont utilisés, la quantité totale desdits éléments est limitée à la valeur maximale de l'un desdits éléments individuels ajoutés.

35 5. Aimant suivant la revendication 1, comprenant en outre au moins un élément complémentaire M, où M représente:

	pas plus de 9,5% de Al,	pas plus de 4,7% de Ti,	
	pas plus de 10,5% de V,	pas plus de 8,5% de Cr,	
40	pas plus de 8,0% de Mn,	pas plus de 5,5% de Zr,	
	pas plus de 5,5% de Hf,	pas plus de 12,5% de Nb,	
	pas plus de 10,5% de Ta,	pas plus de 8,7% de Mo,	
	pas plus de 6,0% de Ge,	pas plus de 2,5% de Sb,	
	pas plus de 3,5% de Sn,	pas plus de 5,0% de Bi,	et
45	pas plus de 4,7% de Ni,	pas plus de 8,8% de W,	

et lorsque deux ou plus de deux desdits éléments M sont utilisés, la quantité totale de M est limitée à la valeur maximale de l'un des éléments individuels M ajoutés.

6. Aimant suivant la revendication 5, dans lequel les particules frittées ont un diamètre moyen du grain de cristal d'environ 1 à 100 µm, des diamètres moyens du grain de cristal jusqu'à 80 µm étant exclus.

7. Procédé suivant la revendication 2, comprenant en outre au moins un élément complémentaire M, où M représente:

	pas plus de 9,5% de Al,	pas plus de 4,7% de Ti,	
	pas plus de 10,5% de V,	pas plus de 8,5% de Cr,	
55	pas plus de 8,0% de Mn,	pas plus de 5,5% de Zr,	
	pas plus de 5,5% de Hf,	pas plus de 12,5% de Nb,	
	pas plus de 10,5% de Ta,	pas plus de 8,7% de Mo,	
	pas plus de 6,0% de Ge,	pas plus de 2,5% de Sb,	
60	pas plus de 3,5% de Sn,	pas plus de 5,0% de Bi,	et
	pas plus de 4,7% de Ni,	pas plus de 8,8% de W,	

et lorsque deux ou plus de deux desdits éléments sont utilisés, la quantité totale de M est limitée à la valeur maximale de l'un des éléments individuels M ajoutés.

8. Procédé suivant la revendication 7, dans lequel le frittage est effectué dans des conditions telles que

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les particules frittées aient un diamètre moyen du grain de cristal de 1 à 100 µm, des diamètres moyens du grain de cristal allant jusqu'à 80 µm étant exclus.

9. Aimant tel que défini dans la revendication 5 ou 6, dans lequel, parmi lesdites impuretés (A), Cu ne représente pas plus de 3,3%, S ne représente pas plus de 2,5%, C ne représente pas plus de 4,0%, P ne représente pas plus de 3,3%, Ca ne représente pas plus de 4,0%, Mg ne représente pas plus de 4,0%, O ne représente pas plus de 2,0% et Si ne représente pas plus de 5,0%, et lorsqu'un ou deux ou plus de deux desdits éléments M et, respectivement, A sont utilisés, la quantité totale de (M+A) est limitée à la valeur maximale de l'un des éléments individuels M et A ajoutés.

10. Procédé suivant la revendication 7 ou 8, dans lequel, parmi lesdites impuretés, Cu ne représente pas plus de 3,3%, S ne représente pas plus de 2,5%, C ne représente pas plus de 4,0%, P ne représente pas plus de 3,3%, Ca ne représente pas plus de 4,0%, Mg ne représente pas plus de 4,0%, O ne représente pas plus de 2,0% et Si ne représente pas plus de 5,0%, et lorsqu'un ou deux ou plus de deux desdits éléments M et, respectivement, A sont utilisés, la quantité totale de (M+A) est limitée à la valeur maximale de l'un des éléments individuels M et A ajoutés.

11. Aimant tel que défini dans la revendication 1, 5 ou 6, dans lequel, en pourcentages atomiques, R représente 12 à 20% et B représente 5 à 18%.

12. Aimant tel que défini dans la revendication 11, dans lequel R représente 12 à 16% et B représente 6 à 18%.

13. Procédé tel que défini dans la revendication 2, 7 ou 8, dans lequel, en pourcentages atomiques, R représente 12 à 20% et B représente 5 à 18%.

14. Procédé tel que défini dans la revendication 13, dans lequel R représente 12 à 16% et B représente 6 à 18%.

15. Aimant tel que défini dans la revendication 1, 5 ou 6, dans lequel R contient 50% ou plus de 50% d'éléments légers des terres rares.

16. Aimant tel que défini dans la revendication 15, dans lequel R contient 50% ou plus de 50% de Nd et/ou de Pr.

17. Aimant tel que défini dans la revendication 16, dans lequel, en pourcentages atomiques, R représente environ 15% et B représente environ 8%.

18. Procédé tel que défini dans la revendication 2, 7 ou 8, dans lequel R contient 50% ou plus de 50% d'éléments légers des terres rares.

19. Procédé tel que défini dans la revendication 18, dans lequel R contient 50% ou plus de 50% de Nd et/ou de Pr.

20. Procédé tel que défini dans la revendication 19, dans lequel, en pourcentages atomiques, R représente environ 15% et B représente environ 8%.

21. Aimant tel que défini dans la revendication 1, 5 ou 6, dans lequel la phase principale est formée par un alliage du type FeBR ayant une structure cristalline principalement tétragonale.

22. Aimant tel que défini dans la revendication 1, 5 ou 6, qui contient 1% en volume ou plus d'une phase riche en terres rares.

23. Aimant tel que défini dans la revendication 1, 5 ou 6, qui a une valeur (BH)_{max} non inférieure à 16 kJ/m³ (2 MGOe).

24. Aimant tel que défini dans la revendication 11, qui a une valeur (BH)_{max} non inférieure à 32 kJ/m³ (4 MGOe).

25. Aimant tel que défini dans la revendication 12, qui a une valeur (BH)_{max} non inférieure à 56 kJ/m³ (7 MGOe).

26. Aimant tel que défini dans la revendication 5 ou 6, dans lequel des éléments complémentaires M sont contenus en proportions ou au-dessous des proportions suivantes, en pourcentages atomiques:

7,8% de Al,	3,8% de Ti,	7,8% de V,	6,9% de Cr,
6,9% de Mn,	4,8% de Zr,	4,5% de Hf,	10,0% de Nb,
8,8% de Ta,	7,6% de Mo,	5,0% de Ge,	2,0% de Sb, et
2,7% de Sn,	4,2% de Bi,	3,8% de Ni	7,9% de W,

et lorsque deux ou plus de deux desdits éléments M sont utilisés, la quantité totale de M est limitée à la valeur maximale de l'un des éléments individuels M ajoutés.

27. Procédé tel que défini dans la revendication 7 ou 8, dans lequel des éléments complémentaires M sont utilisés dans les proportions ou au-dessous des proportions suivantes, indiquées en pourcentages atomiques:

7,8% de Al,	3,8% de Ti,	7,8% de V,	6,9% de Cr,
6,9% de Mn,	4,8% de Zr,	4,5% de Hf,	10,0% de Nb,
8,8% de Ta,	7,6% de Mo,	5,0% de Ge,	2,0% de Sb, et
2,7% de Sn,	4,2% de Bi,	3,8% de Ni	7,9% de W,

et lorsque deux ou plus de deux desdits éléments M sont utilisés, la quantité totale de M est limitée à la valeur maximale de l'un des éléments individuels M ajoutés.

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28. Aimant tel que défini dans la revendication 12, dans lequel des éléments complémentaires M sont présents en proportions ou au-dessous des proportions suivantes exprimées en pourcentages atomiques:

5	3,4% de Al,	1,3% de Ti,	3,4% de V,	1,5% de Cr,
	2,1% de Mn,	1,9% de Zr,	1,7% de Hf,	2,8% de Nb,
	3,0% de Ta,	2,8% de Mo,	1,6% de Ge,	0,5% de Sb, et
	0,7% de Sn,	1,9% de Bi,	1,3% de Ni,	3,7% de W,

et lorsque deux ou plus de deux desdits éléments M sont utilisés, la quantité totale de M est limitée à la valeur maximale de l'un des éléments individuels M ajoutés.

29. Procédé tel que défini dans la revendication 14, dans lequel les éléments complémentaires M sont utilisés en proportions ou au-dessous des proportions suivantes exprimées en pourcentages atomiques:

15	3,4% de Al,	1,3% de Ti,	3,4% de V,	1,5% de Cr,
	2,1% de Mn,	1,9% de Zr,	1,7% de Hf,	2,8% de Nb,
	3,0% de Ta,	2,8% de Mo,	1,6% de Ge,	0,5% de Sb, et
	0,7% de Sn,	1,9% de Bi,	1,3% de Ni,	3,7% de W,

et lorsque deux ou plus de deux desdits éléments M sont utilisés, la quantité totale de M est limitée à la valeur maximale de l'un des éléments individuels M ajoutés.

30. Aimant tel que défini dans la revendication 26, qui a une valeur Br non inférieure à 0,4 tesla (4 kG).

31. Aimant tel que défini dans la revendication 28, qui a une valeur Br non inférieure à 0,6 tesla (6 kG).

32. Aimant tel que défini dans la revendication 5 ou 6, dans lequel M est un ou plusieurs des éléments choisis dans le groupe comprenant V, Nb, Ta, Mo, W, Cr et Al.

33. Procédé tel que défini dans la revendication 2, 7 ou 8, dans lequel le frittage est effectué à une température de 900 à 1200°C.

34. Procédé tel que défini dans la revendication 33, dans lequel le frittage est effectué dans une atmosphère non oxydante ou réductrice.

35. Procédé tel que défini dans la revendication 34, dans lequel ladite atmosphère est le vide ou une pression réduite, ou un gaz inerte d'une pureté égale ou supérieure à 99,9%, sous une pression de 133 à 101 325 Pa (1—760 torrs).

Fig. 1

$(92-x)\text{Fe}-8\text{B}-x\cdot\text{Nd}$

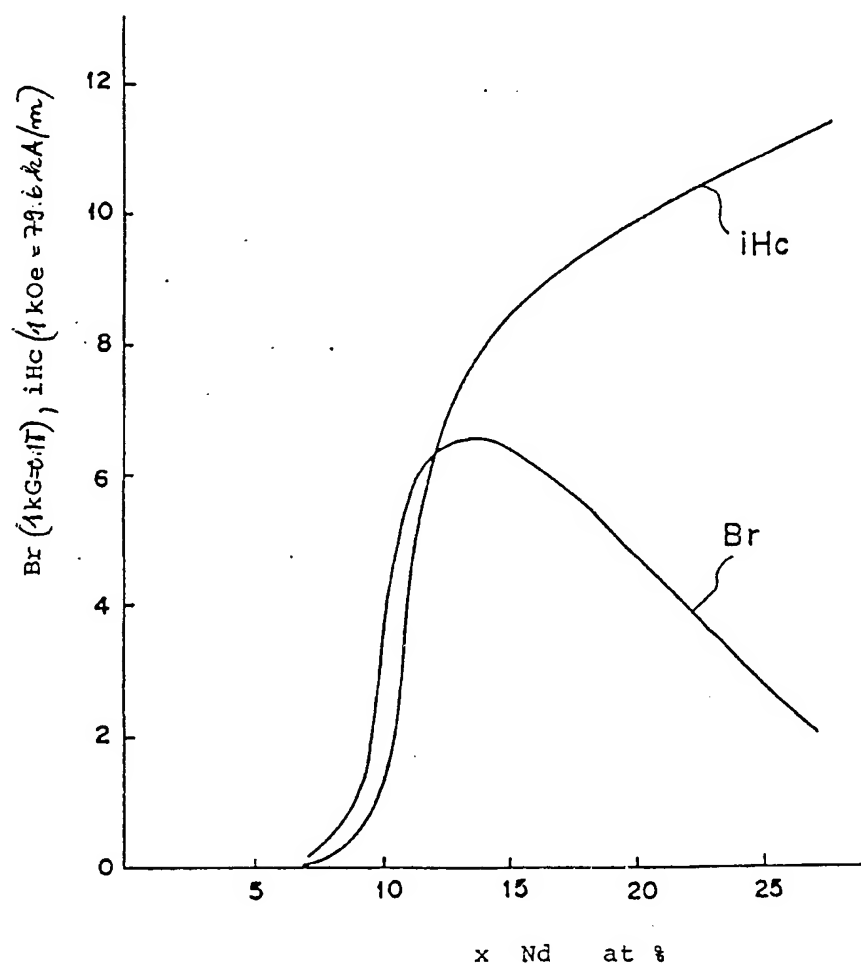


Fig. 2

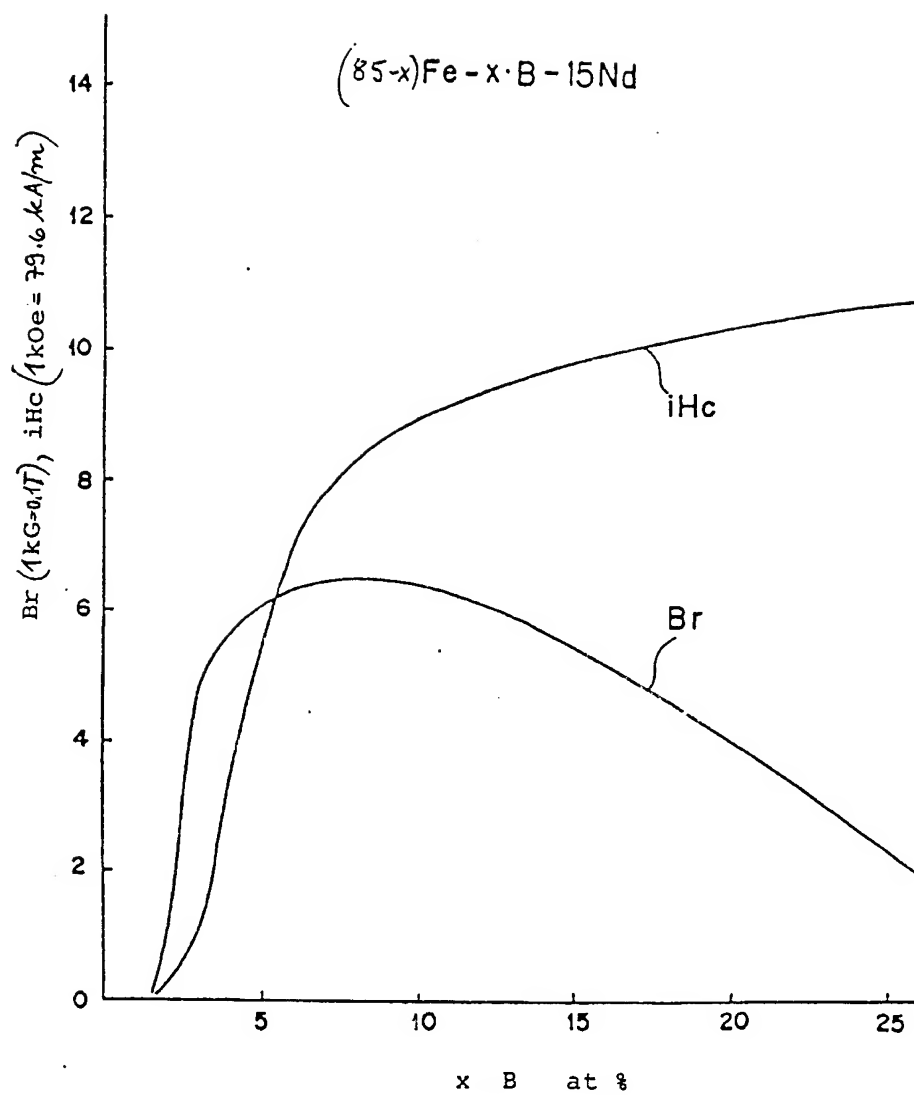


Fig. 3

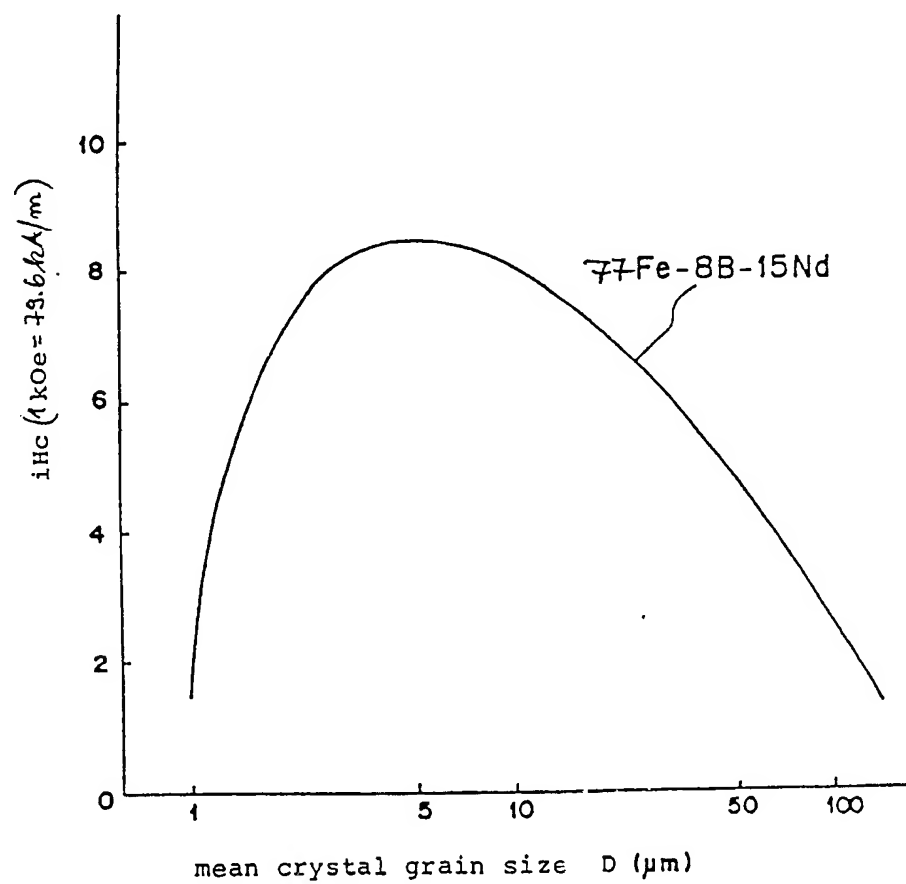


Fig. 4

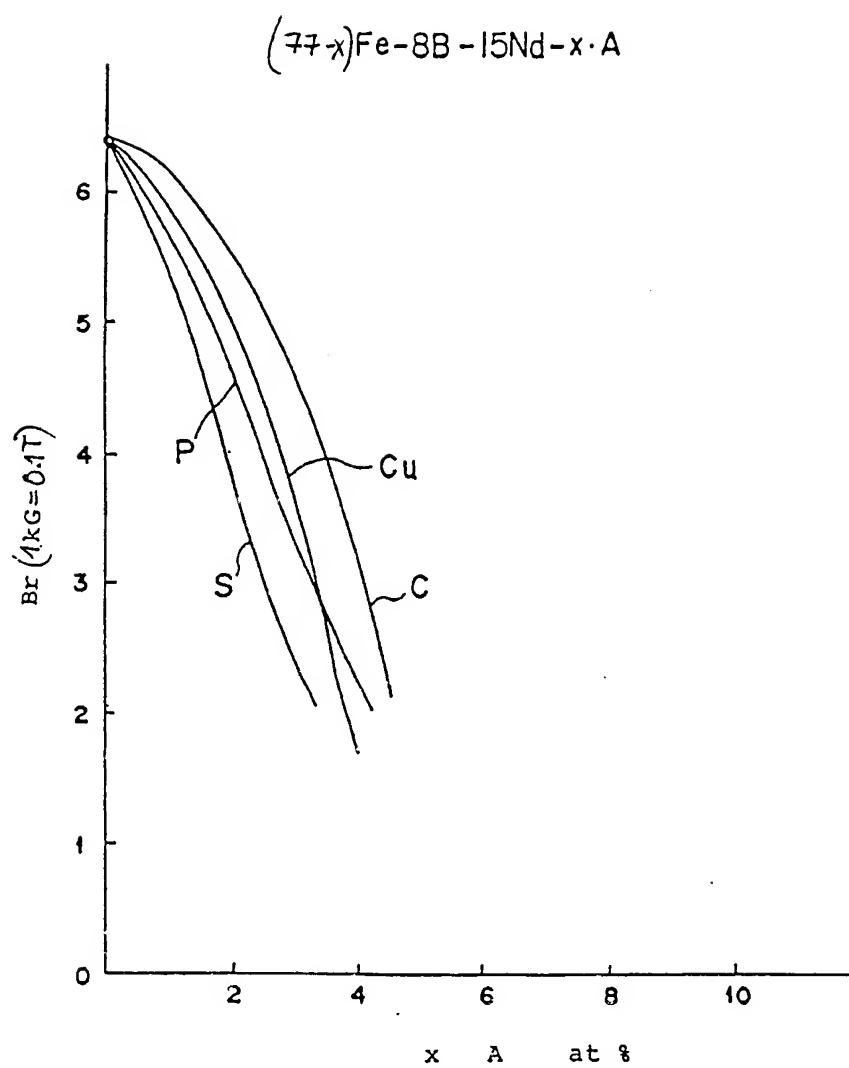


Fig. 5

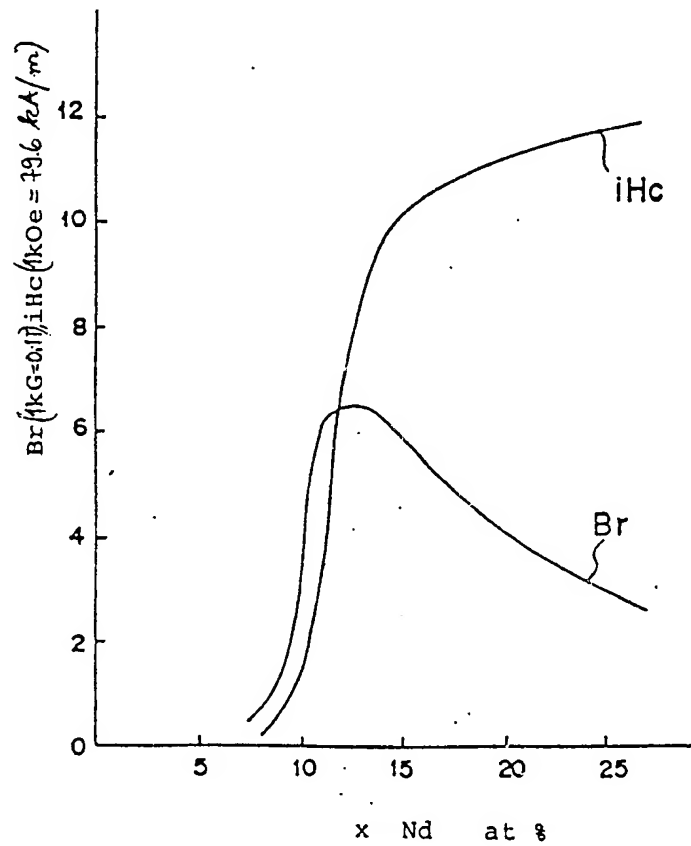
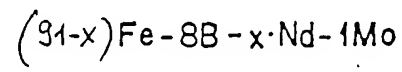


Fig.6

$(84-x)\text{Fe} - x\cdot\text{B} - 15\text{Nd} - 1\text{Mo}$

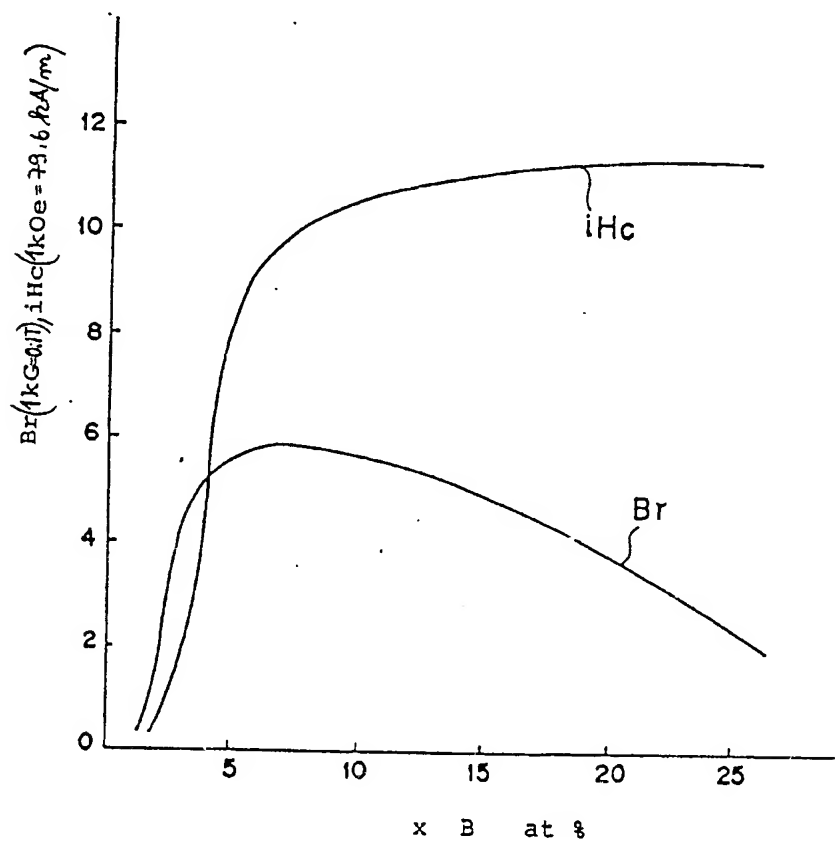


Fig.7

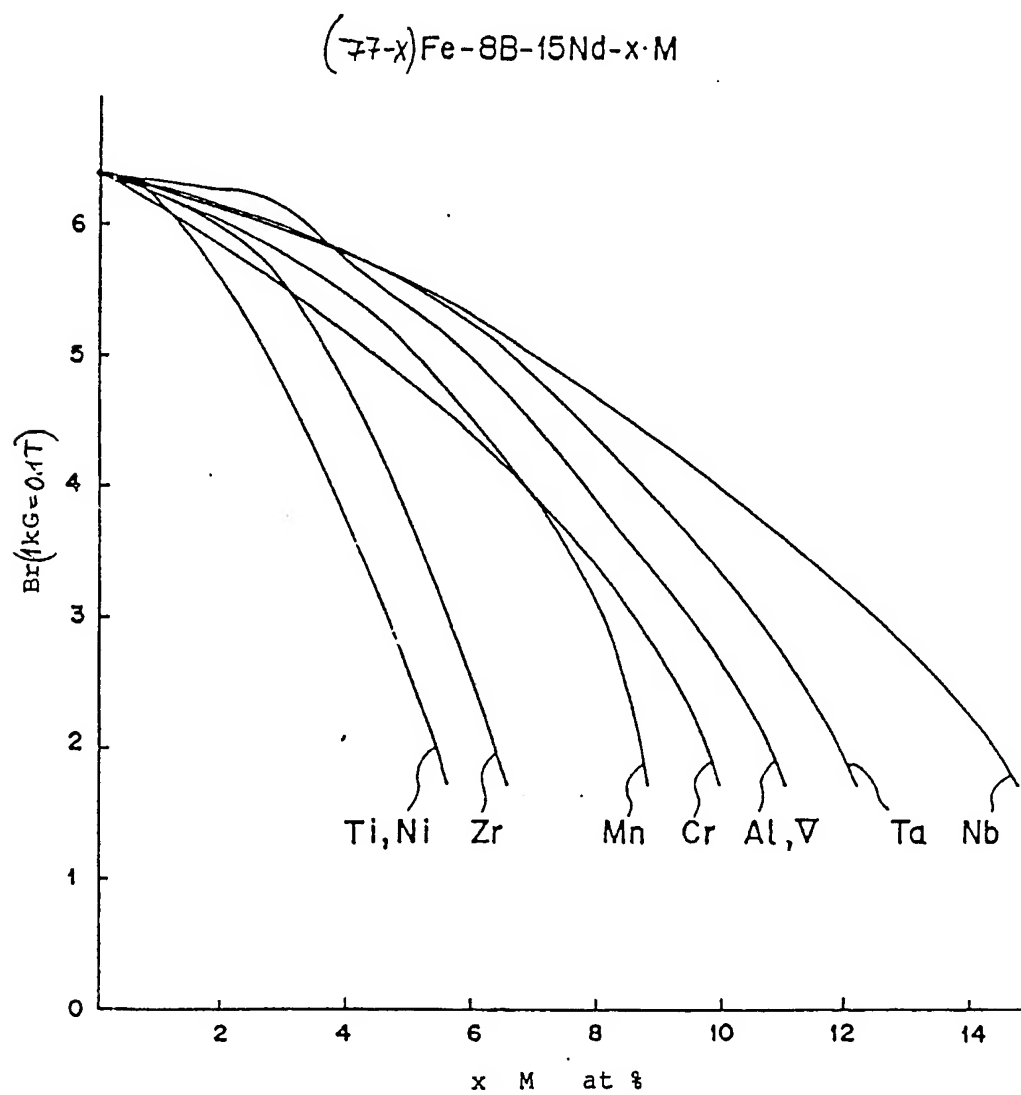


Fig.8

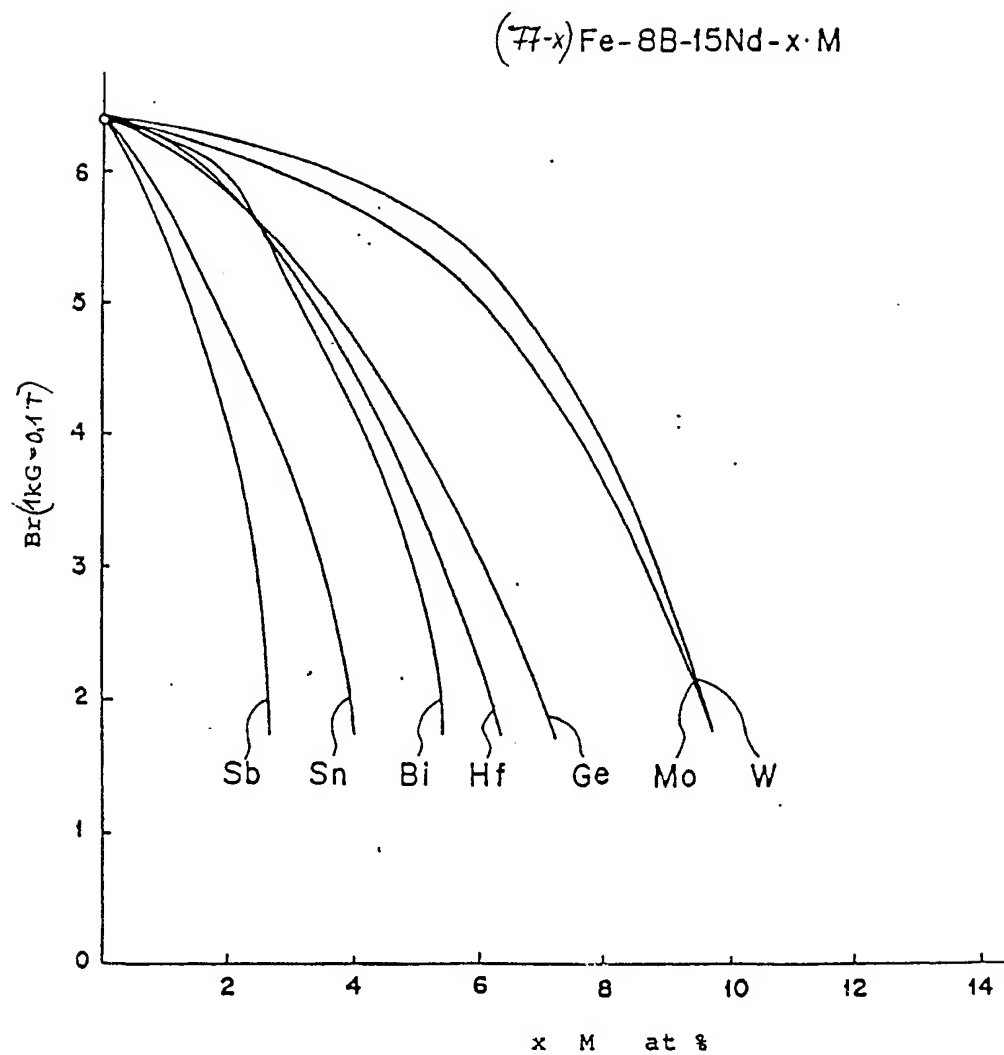
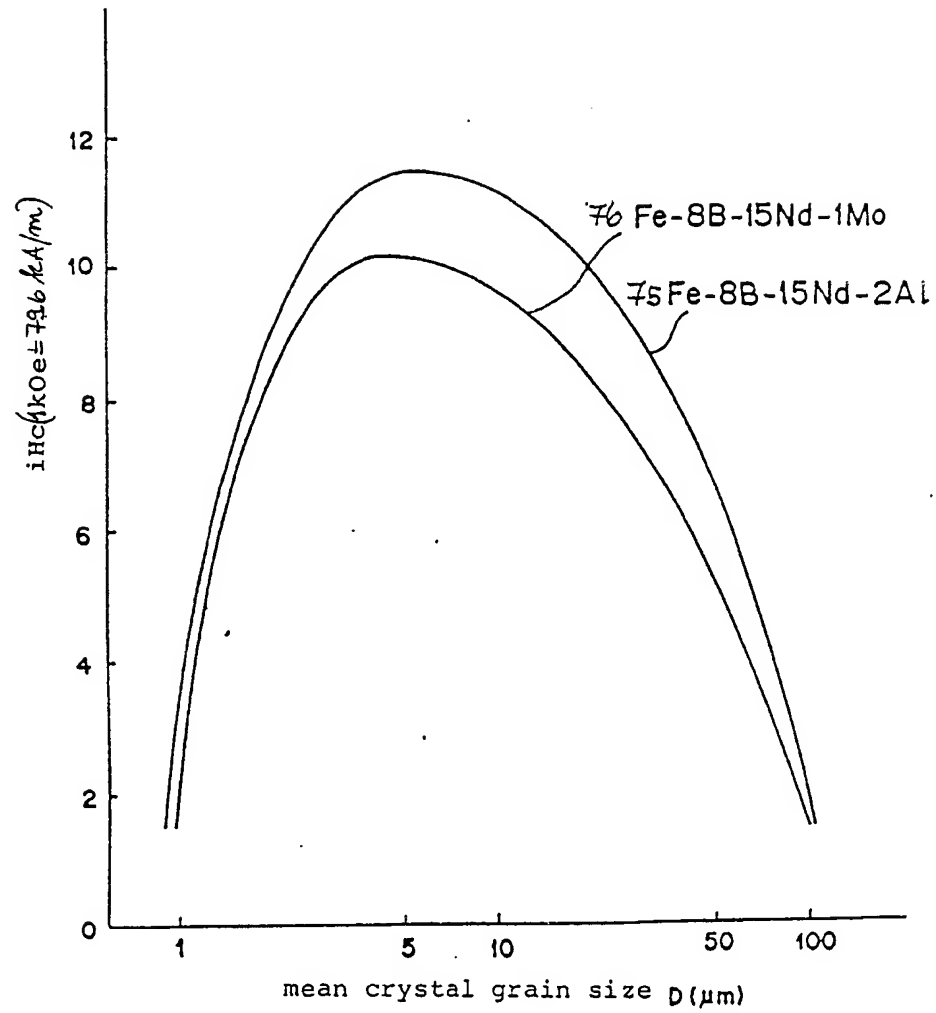


Fig.9





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